Ferroelectric domain scaling and switching in ultrathin $BiFeO_3$ films deposited on vicinal substrates

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14. ABSTRACT

We report on electrically switchable polarization and ferroelectric domain scaling over a thickness range of 5?100 nm in BiFeO3 films deposited on [110] vicinal substrates. The BiFeO3 films of variable thickness were deposited with SrRuO3 bottom layer using the pulsed laser deposition technique. The domains are engineered into preferentially oriented patterns due to substrate vicinality along the [110] direction. The domain width scales closely with the square root of film thickness, in agreement with the Landau?Lifschitz?Kittel (LLK) law. Switching spectroscopy piezo-response force microscopy provides clear evidence for the ferroelectric switching behavior in all the films.

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Ferroelectric domain scaling and switching in ultrathin $BiFeO_3$ films deposited on vicinal substrates

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Abstract. We report on electrically switchable polarization and ferroelectric domain scaling over a thickness range of 5–100 nm in $BiFeO_3$ films deposited on [110] vicinal substrates. The $BiFeO_3$ films of variable thickness were deposited with $SrRuO_3$ bottom layer using the pulsed laser deposition technique. The domains are engineered into preferentially oriented patterns due to substrate vicinality along the [110] direction. The domain width scales closely with the square root of film thickness, in agreement with the Landau–Lifschitz–Kittel (LLK) law. Switching spectroscopy piezo-response force microscopy provides clear evidence for the ferroelectric switching behavior in all the films.

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Contents

1. Introduction

Recent studies on $BiFeO_3$ (BFO) thin films are guided by two aspects: tetragonality and vicinality. BFO films deposited on large lattice mismatched substrates such as $LaAlO_3$ show monoclinically distorted tetragonal structure [1, 2]. The stabilization of the pure tetragonal phase remains elusive, although theoretical calculations suggest strain [3] and electric field [4] induced phase stabilization or transition. We have reported on the ferroelectric behavior of strain relaxed $BiFeO_3$ thin films on lattice mismatched substrates [5] and have also pursued the tetragonality issue for the fundamental understanding using piezo-response force microscopy (PFM) and polarized Raman spectroscopy techniques [6, 7]. On the other hand, deposition of BFO films on vicinal substrates can assist in the engineering of ferroelectric domain structure [8, 9]. Such films have two domain variants as compared to four domain variants observed in thin films deposited on plain substrates. As a consequence, ferroelectric switching is better on vicinal substrates. We reported the reduction of coercive field through the domain engineering approach [10]. BFO films deposited on $SrTiO_3$ substrates with 4° miscut along the [110] direction exhibited a higher polarization value and a significantly reduced coercive field. It is clear that the domain structure plays a vital role in governing technologically important parameters such as polarization and coercive field. However, a detailed study of the nature of such domains with broken symmetry has not been reported so far.

Universally, ferroelectric or ferromagnetic domains follow the Landau, Lifshitz and Kittel (LLK) law wherein the domain width scales with the square root of film thickness [11]. The original scaling law, also referred to as the 'Kittel law', was extended to ferroelastic domains in thin films by Roytburd [12]. A detailed account of domain studies has recently been reviewed by Catalan *et al* [13]. In the particular case of BFO thin films deposited on plain $SrTiO_3$ substrates, Catalan *et al* [14] reported deviation from the LLK law. Such a deviation was primarily attributed to the fractal dimensionality of domains in the thin film deposited on plain [100] substrates. In contrast, the first principle-based study of ultrathin BFO films by Prosandeev *et al* [15] suggested that the Kittel law is followed in the case of straight-walled domains. They argued that the interaction between tilting of oxygen octahedra around domain walls and magnetoelectric coupling plays an important role in the validation of the Kittel law. For this work, we deposited 5–100 nm thickness BFO films on $SrTiO_3$ substrates with 4° miscut along the [110] direction. The [110] direction of miscut is the requisite criterion to break domain symmetry through sawtooth step pattern [10]. We verified the structural quality of the

films using the x-ray diffraction (XRD) technique. Crystallographically oriented domains with variable dimensions were observed using PFM. We confirmed the variation of the domain size with film thickness in agreement with the LLK law. We also provide unambiguous evidence for ferroelectricity in ultrathin (up to 5 nm) BFO films using the advanced switching spectroscopy piezo-response force microscopy (SSPFM) technique.

2. Experimental details

We have deposited $BiFeO_3$ (BFO) thin films of variable thickness in the range 5–100 nm on (100) $SrTiO_3$ substrates with 4° miscut along the [110] direction. The BFO films with $SrRuO_3$ (SRO) bottom layer were deposited sequentially using the pulsed laser deposition method [10, 16]. The crystalline quality and out of plane lattice parameters were determined using x-ray diffraction (X'pert Pro. Panalytical) with CuK_α radiation. The surface topography and domain structure were revealed using atomic microscopy and PFM under ambient conditions. For this purpose, the commercial Scanning Probe Microscope (Cypher, Asylum Research) equipped with a Pt-coated conducting tip (AC240TM, Olympus) was operated at the resonance frequency of about 260 kHz and the ac bias amplitude of 2 V. The same setup was augmented to carry out advanced SSPFM measurements [17, 18]. We used a 25×25 grid on $2\,\mu m \times 2\,\mu m$ scan area to map the local polarization switching with variable tip bias between +10 and −10 V.

3. Results and discussion

3.1. Structural analysis

The XRD patterns of 100, 50, 20 and 10 nm BFO films deposited with 40 nm SRO bottom layer on STO substrates with 4° miscut along the [110] direction are shown in figure 1(a). The inset shows clearly distinguishable (100) peaks. The highly oriented textured growth of the films is evident from the appearance of (00l) peaks. The representative omega and phi scans shown in figures 1(b) and (c) clearly reveal the crystalline quality and epitaxial nature of these films. The full-width at half-maxima (FWHM) values for the omega scan were around 0.04° and the phi scan exhibited fourfold symmetry. The out of plane lattice parameters determined from XRD data were 4.01, 4.05, 4.06 and 4.08 Å for the 100, 50, 20 and 10 nm thickness films, respectively. The bulk value of the psudo-cubic lattice parameter is 3.96 Å. However, the substrate-induced in-plane compression of unit cells causes out of plane elongation. It has been reported that the lattice parameter varies with the substrates [19], with film thickness [20] and with operating oxygen pressure [21]. Our films seem somewhat constrained with reducing thickness, which is in agreement with the reported behavior for other miscut substrates [8].

3.2. Ferroelectric domain scaling

Surface topography scans of $2\,\mu m \times 2\,\mu m$ areas of 100, 50, 20, 10 and 5 nm thickness BFO films are shown in figures 2(a)–(e), respectively. In general, BFO films are known to grow in the three-dimensional (3D) island growth mode [8]. However, the step flow growth mode has been reported on orthorhombic $DyScO_3$ substrates [22], on the miscut substrates [8, 19] and possibly with growth under optimized oxygen pressure [21]. The parallel steps with larger width resulting from step bunching were reported on the substrates with 4° miscut along the [100]

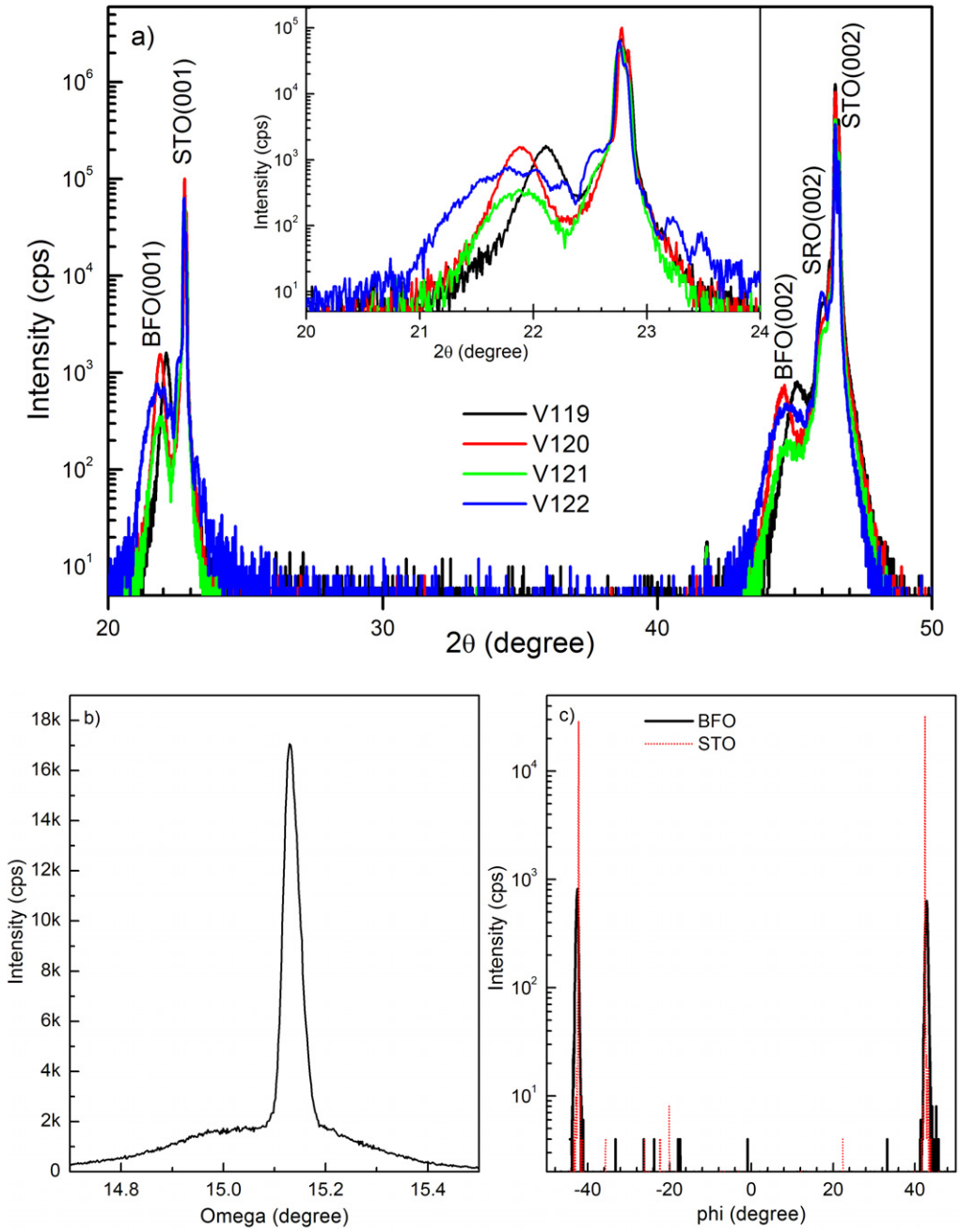

Figure 1. (a) XRD patterns for 100 nm (V119), 50 nm (V120), 20 nm (V121) and 10 nm (V122) $BiFeO_3$ films deposited with $SrRuO_3$ bottom layer on [110] vicinal $SrTiO_3$ substrates. Inset: resolved (001) peaks. Representative omega (b) and phi (c) scans to reveal crystalline and epitaxial nature.

direction [8, 19]. On the other hand, when the miscut angle is along the [110] direction, as in the present case, the steps have a sawtooth pattern. The parallel steps promote a nano-wire kind of growth along the steps or perpendicular to the miscut direction. The sawtooth steps may promote nano-particle kind of growth on the triangular steps [10]. Further, step bunching is

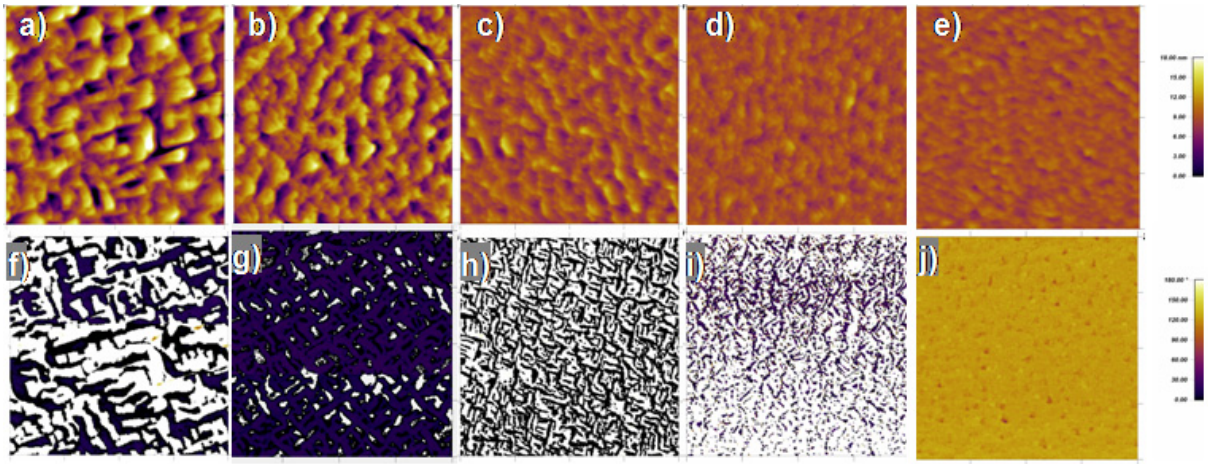

Figure 2. The surface topography scans (a–e) and corresponding ferroelectric domain structures (f–j) of $2\,\mu\text{m} \times 2\,\mu\text{m}$ areas of 100, 50, 20, 10 and 5 nm thickness $BiFeO_3$ films, respectively.

possible, making the sawtooth patterns more washed out. In figures 2(a)–(e), the topographical patterns show traces of sawtooth step flow growth. They are similar except that the grain size becomes smaller with decreasing thickness of the films.

The evolution of ferroelectric domains with variant film thickness, recorded through vertical PFM, is shown in figures 2(f)–(j). The black and white contrasts in these images indicate polarization components pointing in the down and up directions, respectively. It has been documented that the BFO films have four and two polarization variants when deposited on exact and [100] vicinal substrates, respectively [8, 19]. The domains have large size and stripe patterns running perpendicular to the vicinal direction. Jang *et al* [8] attributed such a pattern formation to the relaxation of elastic-strain energy of the films on step surfaces without the need for two additional domain variants. However, the vicinality along the [110] direction yields a sawtooth step pattern, which may break the symmetry of stripe domains. It results in two variant domains with a pattern intermediate between stripe and fractal. These domains have crystallographic orientation and straight wall features such as stripe domains. However, the orientation is confined to smaller areas due to sawtooth steps of the vicinal substrate. Such domains can have double advantages, better polarization due to two variants and better switchability, resulting from step-edge dislocations [10]. Similar types of small bunches of striped ferroelastic domains are reported in compressively strained $TbMnO_3$ films deposited on $SrTiO_3$ substrates [23].

An important feature of these domain patterns is the systematic reduction of domain size with thickness. The contrast patterns with reducing dimensions were seen in up to 10 nm thickness films. The 5 nm thickness film did not show the signature of domain formation, probably owing to crosstalk interference. On plain STO substrates, Daumont *et al* [24] could not detect the contrast in 12 nm thickness BFO films, whereas Catalan *et al* [14] reported fractal domains in up to 7 nm thickness films. They also reported that the average domain size departed from the classic LLK square root dependence on film thickness with the scaling exponent $\gamma = 0.59$. The variation of domain width as a function of film thickness for BFO films on

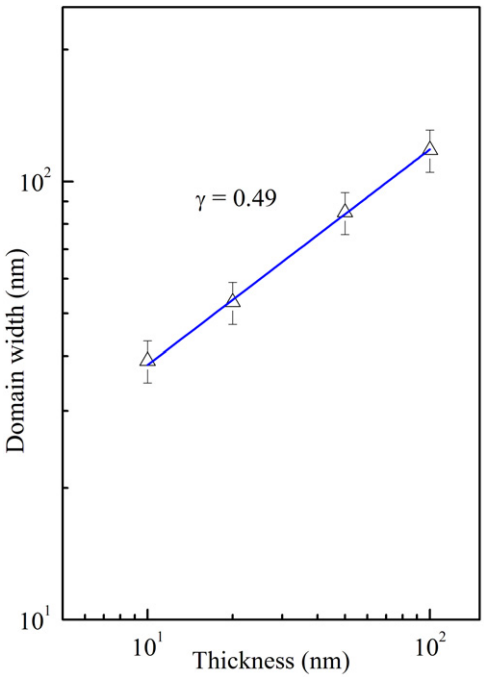

Figure 3. The variation of domain width as a function of film thickness for BFO films deposited on [110] vicinal substrates.

vicinal substrates is shown in figure 3. The curve fitting to the law

$$w = Ad^{\gamma}, \tag{1}$$

where w is the average domain width and d is the film thickness, gave the scaling exponent value $\gamma = 0.49 \pm 0.05$, which is very close to the LLK value of 0.5 [11]. However, it is smaller than the value 0.59 reported by Catalan *et al* [14] for BFO thin films on plain substrate. On the plain substrate the domains in the thick film are larger with four polarization variants. The reduction of film thickness can cause a rapid reduction in domain size, making the scaling exponent greater than 0.5. On the other hand, the use of [110] vicinal substrates yields small bunches of preferentially aligned domains. A low crystal anisotropy and pinning defects may be responsible for such appearance [25]. The terraces, steps, kinks, etc on [110] vicinal substrates can provide ample sites for the domain formations. Therefore, the domain size reduction with thickness may not be as rapid as in the case of plain substrates. The square root dependence of equation (1) can also be rewritten as [26]

$$w = (G/\delta)^{1/2} d^{\gamma}, \tag{2}$$

where G is an adimensional parameter and δ is the domain wall thickness. The constant G is less dependent on materials. An accurate estimate of G is possible for regular stripe domains with thick domain wall. In the present case, however, the domains are of intermediate type with very small wall thickness. Therefore, it is difficult to estimate the G value accurately. Nevertheless, the combined value of $(G/\delta)^{1/2}$ that corresponds to the y-intercept of the fitted curve in figure 3 is 12.3. Thus, the [110] vicinal substrate assists in the growth of two variant, small-size domains which follow LLK scaling closely. Such domains are more vulnerable to applied electric field and can be switched with lower field [10]. Prosandeev *et al* [15] have predicted that the Kittel

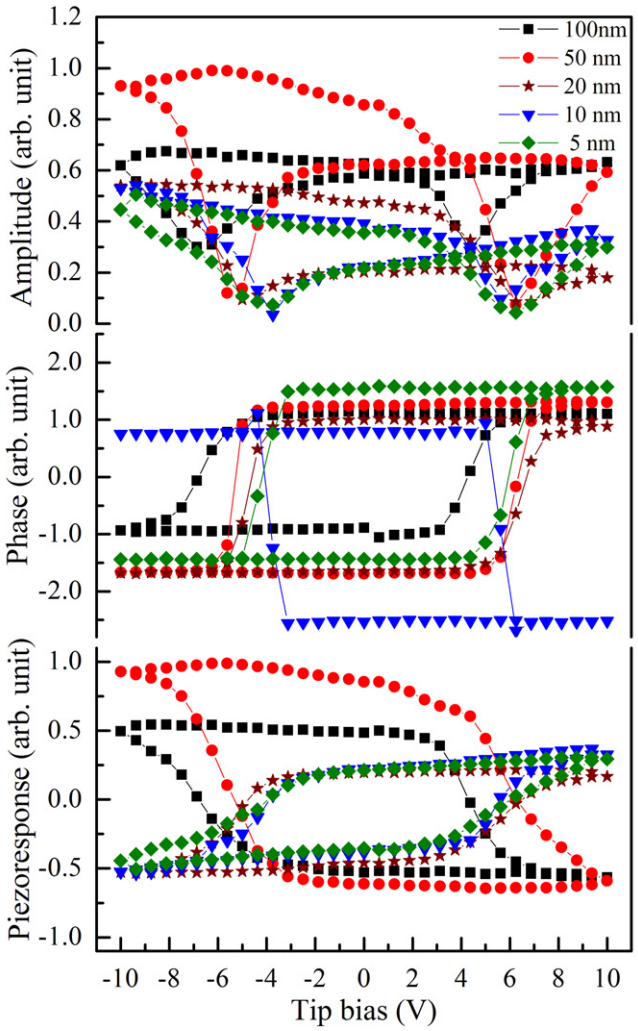

Figure 4. Switching behavior of BFO films of variable thickness as revealed through SS-PFM: (a) amplitude, (b) phase and (c) piezo-response signals as a function of tip bias.

law can be obeyed in BFO films containing stripe domains rather than fractal states. Our study confirmed that the scaling is indeed followed for intermediate types of domains.

3.3. Ferroelectric switching behavior

The electrical switching behavior of our films is shown in figures 4(a)–(c). The characteristic butterfly loops were observed in amplitude signals of all the BFO films including the 5 nm thickness film (figure 4(a)). Figure 4(b) shows the phase signal indicative of a clear switching behavior. The collective piezo-response shown in figure 4(c) also confirms that clear and complete polarization switching can be accomplished within the bias of ± 10 V. It gives unambiguous evidence for the occurrence of ferroelectricity in BFO films as thin as 5 nm deposited on vicinal substrates. The ferroelectricity remained mostly unaffected throughout the grid of measurement and over multiple cycles of voltage applications. Although Bea *et al* [27]

observed PFM pattern for 2 nm thickness BFO films deposited on plain substrate, they have not reported switching behavior. Moreover, the use of vicinal substrate in the present study is more promising to obtain low-voltage switching [10]. It is difficult to quantify the magnitude of polarization and coercive field from SSPFM data alone [18]. The macroscopic measurements on thick films indicated that the effective switching of $BiFeO_3$ films on [110] vicinal substrates can be accomplished with a lower voltage or reduced coercive field. The reported values of coercive field for BFO thin films deposited on plain substrates are mostly around 200 kV cm^{-1}, whereas on [110] vicinal substrate it is 78 kV cm^{-1} [10]. Therefore, the 5 nm $BiFeO_3$ films deposited on [110] vicinal substrate may satisfy the dimensional constraints for tunneling as well as the existence of switchable ferroelectricity. The current device demand not only requires reliable switching behavior, but also switching at a much lower energy. This work provides a clear demonstration of the possibility of achieving such an objective through the use of vicinal substrates.

4. Conclusions

We deposited 5–100 nm thickness $BiFeO_3$ films on vicinal $SrTiO_3$ substrates with 4° miscut along the [110] direction. The epitaxial and constrained films showed traces of sawtooth step flow growth in topographical features. The PFM revealed two variant, preferentially aligned domains. The domain width scaling with film thickness closely followed the LLK law. It endorsed the fact that the universal LLK law is valid for preferentially aligned ferroelectric domains in BFO thin films. A clear switching was observed through SSPFM in all the films including the ultrathin 5 nm film. Such domain engineered ultrathin films have better potential for the fabrication of multiferroic tunnel junctions.

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References

[1] Bea H *et al* 2009 Evidence for room-temperature multiferroicity in a compound with giant axial ratio *Phys. Rev. Lett.* **102** 217603
[2] Zeches R J *et al* 2009 A strain-driven morphotropic phase boundary in $BiFeO_3$ *Science* **326** 977
[3] Hatt A J, Spaldin N and Ederer C 2010 Strain-induced isosymmetric phase transition in $BiFeO_3$ *Phys. Rev.* B **81** 054109
[4] Lisenkov S, Rahmedov D and Bellaiche L 2009 Electric-field-induced paths in multiferroic $BiFeO_3$ from atomistic simulations *Phys. Rev. Lett.* **103** 047204
[5] Shelke V, Srinivasan G and Gupta A 2010 Ferroelectric properties of $BiFeO_3$ thin films deposited on substrates with large lattice mismatch *Phys. Status Solidi RRL* **4** 79
[6] Mazumdar D, Shelke V, Iliev M, Jesse S, Kumar A, Kalinin S V, Baddorf A P and Gupta A 2010 Nanoscale switching characteristics of nearly tetragonal $BiFeO_3$ thin films *Nano Lett.* **10** 2555

[7] Iliev M N, Abrashev M V, Mazumdar D, Shelke V and Gupta A 2010 Polarized Raman spectroscopy of nearly tetragonal $BiFeO_3$ thin film *Phys. Rev.* B **82** 014107
[8] Jang H W, Ortiz D, Baek S H, Folkman C M, Das R R, Shafer P, Chen Y, Pan X, Ramesh R and Eom C B 2009 Domain engineering for enhanced ferroelectric properties of epitaxial (001) BiFeO thin films *Adv. Mater.* **21** 817
[9] Chu Y H, Cruz M P, Yang C H, Martin L W, Yang P L, Zhang J X, Lee K, Yu P, Chen L Q and Ramesh R 2007 Domain control in multiferroic $BiFeO_3$ through substrate vicinality *Adv. Mater.* **19** 2662
[10] Shelke V, Mazumdar D, Srinivasan G, Kumar A, Jesse S, Kalinin S V, Baddorf A P and Gupta A 2011 Reduced coercive field in $BiFeO_3$ thin films through domain engineering *Adv. Mater.* **23** 669
[11] Kittel C 1949 Physical theory of ferromagnetic domains *Rev. Mod. Phys.* **21** 541
[12] Roytburd A L 1976 Equilibrium structure of epitaxial layer *Phys. Status Solidi* a **37** 329
[13] Catalan G, Seidel J, Ramesh R and Scott J F 2012 Domain wall nanoelectronics *Rev. Mod. Phys.* **84** 119
[14] Catalan G, Bea H, Fusil S, Bibes M, Paruch P, Barthelemy A and Scott J F 2008 Fractal dimension and size scaling of domains in thin films of multiferroic $BiFeO_3$ *Phys. Rev. Lett.* **100** 027602
[15] Prosandeev S, Lisenkov S and Bellaiche L 2010 Kittel law in $BiFeO_3$ ultrathin films: a first-principles-based study *Phys. Rev. Lett.* **105** 147603
[16] Shelke V, Harshan V N, Kotru S and Gupta A 2009 Effect of kinetic growth parameters on leakage current and ferroelectric behavior of $BiFeO_3$ thin films *J. Appl. Phys.* **106** 104114
[17] Jesse S, Lee H N and Kalinin S V 2006 Quantitative mapping of switching behavior in piezoresponse force microscopy *Rev. Sci. Instrum.* **77** 073702
[18] Kalinin S V *et al* 2010 Defect-mediated polarization switching in ferroelectrics and related materials: from mesoscopic mechanisms to atomistic control *Adv. Mater.* **22** 314
[19] Das R R *et al* 2006 Synthesis and ferroelectric properties of epitaxial $BiFeO_3$ thin films grown by sputtering *Appl. Phys. Lett.* **88** 242904
[20] Kim D H, Lee H N, Biegalski M D and Christen H M 2008 Effect of epitaxial strain on ferroelectric polarization in multiferroic $BiFeO_3$ films *Appl. Phys. Lett.* **92** 012911
[21] You L, Chua N T, Yao K, Chen L and Wang J 2009 Influence of oxygen pressure on the ferroelectric properties of epitaxial $BiFeO_3$ thin films by pulsed laser deposition *Phys. Rev.* B **80** 024105
[22] Chu Y H *et al* 2006 Nanoscale domain control in multiferroic $BiFeO_3$ thin films *Adv. Mater.* **18** 2307
[23] Daumont C J M, Mannix D, Venkatesan S, Catalan G, Rubi D, Kooi B J, Hosson De J Th M and Noheda B 2009 Epitaxial $TbMnO_3$ thin films on $SrTiO_3$ substrates: a structural study *J. Phys.: Condens. Matter* **21** 182001
[24] Daumont C J M, Farokhipoor S, Ferri A, Wojdel J C, Iniguez J, Kooi B J and Noheda B 2010 Tuning the atomic and domain structure of epitaxial films of multiferroic $BiFeO_3$ *Phys. Rev.* B **81** 144115
[25] Catalan G and Scott J F 2009 Physics and applications of bismuth ferrite *Adv. Mater.* **21** 2463
[26] Scott J F 2006 Nanoferroelectrics: statics and dynamics *J. Phys.: Condens. Matter* **18** R361
[27] Bea H, Fusil S, Bouzehouane K, Bibes M, Sirena M, Herranz G, Jacquet E, Contour J P and Barthelemy A 2006 Ferroelectricity down to at least 2 nm in multiferroic $BiFeO_3$ epitaxial thin films *Japan. J. Appl. Phys.* **45** L187